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(54) **Hair colouring composition comprising clay**

(57) A rinse off colouring composition comprises:

(i) a clay having a net positive or negative charge at its surface; and

(ii) an agent capable of imparting a colour to hair.
The agent has a net charge which is opposite from

the charge on the surface of the clay. The compositions have good colour delivery to hair and reduced colouration of skin relative to colouration of hair.

Description

[0001] This invention relates to a colouring composition, to a method of producing the composition, to a method of colouring hair using the composition and to the use of a clay.

[0002] Traditional hair colouring compositions (also called colorants) can be permanent, semi-permanent or temporary in nature.

[0003] Permanent colorants use oxidative dyes and generally comprise two components; a mixture of dye precursors and a developer solution that initiates the formation of coloured dye molecules and enables them to penetrate into the hair fibre. These systems take the form of a treatment which is applied every four to eight weeks to cover outgrowth. The treatment involves the mixing of the two components, the application of the mixture to the hair and a finite period of time during which the colorant is left on the hair to take effect. As such, permanent hair colouring requires a significant amount of time and effort from the consumer. Furthermore, the treatment is non-specific to hair and hence requires gloves to protect the hands from staining during use and permanent hair colourants can also lead to a significant amount of scalp staining if the consumer does not apply the product with great care.

[0004] Semi-permanent colorants are generally single component mixtures that contain dyes, especially nitro dyes, which because of their small size can penetrate the hair and impart colour. These products also require a finite amount of contact time with the hair and are, non-specific, again requiring the use of gloves and with the potential of adverse scalp staining.

[0005] Furthermore, permanent colorants and semi-permanent colorants cannot be used on a regular, particularly daily, basis due to the toxicity of the dyes and dye precursors.

[0006] Finally, temporary dyes are generally large molecules that interact with the hair surface via adsorption processes. However, these are also non-specific in colour delivery and in many cases are not water-fast. Temporary colours are usually leave on systems and as such require the user to apply the product and then wait some period of time until it has dried. This process is both time consuming and inconvenient since the product must be applied once the consumer has finished the normal hair care regimen. Temporary colourants also suffer the limitation of being easily rubbed off onto clothing and pillows.

[0007] It is desirable to produce hair colouring compositions that have reduced skin staining and a higher relative selectivity for colouring hair instead of skin. It would also be desirable to provide compositions that can be used on a daily basis, for example by delivery from a shampoo or conditioner. However, existing hair colouring technology cannot be directly applied to provide such compositions for the reasons given above, particularly skin staining.

[0008] It is known that clays can be used in hair colorant compositions.

[0009] For example, compositions for non-permanently or semi-permanently colouring hair are disclosed in US 5,110,318. The compositions contain from 5% to 25% of a clay and require the treated hair to be heated such that the composition dries to a hard and flaky state. The document exemplifies compositions in which an anionic or neutral dye is employed with an anionic clay. Furthermore, the document teaches away from using substantial amounts of cationic components in the compositions "as an excess amount will complex with the anionic colouring components" having the effect of "reducing the effectiveness of the clay-based compositions to colour hair" (column 6 of the document). There is no mention in the document of the problems of skin staining.

[0010] Temporary hair dye compositions containing clays are described in JP-A-11292744. Anionic or neutral dyes are used together with anionic clays.

[0011] Mechanistic studies have been carried out on combinations of anionic clays with cationic dyes. The term anionic clays and related terms, as used herein, refers to clays which are themselves anionic in nature ie, the clays themselves are negatively charged and are capable of exchanging cations. Examples of such studies are described in, for instance: Miyamoto et al, "Adsorption and aggregation of a cationic cyanine dye on layered clay minerals", *Appl Clay Sci*, 16, (3-4), 161-170, March 2000; Iwasaki et al, "Intercalation characteristics of 1,1'-diethyl-2,2'-cyanine and other cationic dyes in synthetic saponite: Orientation in the interlayer", *Clay Miner*, 48, (3), 392-399, June 2000; Arbeloa et al, "The hydrophobic effect on the adsorption of rhodamines in aqueous suspensions of smectites. The rhodamine 3B Laponite B system", *Langmuir*, 14, (16), 4566-4573, August 4 1998. There is no mention in these documents of the colouring of hair and none of the compositions disclosed in these documents contains components typically present in hair colouring compositions such as perfume and surfactant.

[0012] DE-A-4020272 discloses a pigment based on a layered double hydroxide. The pigment is said to have application in a number of areas, including cosmetics. However, there is no suggestion that the pigment could be used in compositions for treating hair and certainly no indication that the pigment could be used to dye hair in a rinse off composition. The compositions are clearly intended to provide colour to a particular product and it is not the intention to allow transfer of that colour to other materials, such as hair.

[0013] JP-A-54-064644 describes a red pigment for use in cosmetics which is obtained by adsorbing a reaction product of the cationic dye, Rhodamine B, with an anionic dye to a clay material. Again, there is no suggestion that the pigment could be used to colour hair in a rinse off composition. Instead, the aim of the compositions is stated as

being to prevent colour transfer and to have reduced dyeability.

[0014] US 4402698 discloses a two stage process for dyeing hair. In the first stage, a barrier material is applied to protect the skin and a dye is applied in a subsequent second stage. The barrier material, which may be a clay, acts as a physical barrier to prevent the dye from contacting the scalp. There is no teaching of a single composition that contains both a dye and a clay

[0015] There remains a need for colouring compositions that act in a more selective manner than conventional compositions ie they cause relatively less colouring of the skin compared to the hair. It is preferable that the compositions have the further advantages of being able to impart colour to hair from a hair conditioner or shampoo on a daily basis, with good water-fastness, preferably with a degree of reversibility (ie, the dye can be washed off with shampoo).

[0016] Accordingly the present invention provides a rinse off hair colouring composition comprising:

(i) a clay having a net positive or negative charge at its surface;

(ii) an agent capable of imparting a colour to hair; and

(iii) a perfume and/or a surfactant,

wherein the agent has a net charge which is opposite from the charge on the surface of the clay.

[0017] In another aspect the invention provides a method of producing a composition of the invention which comprises dispersing the clay in an aqueous liquid to form a dispersion and then bringing the agent into contact with the dispersion

[0018] Yet another aspect of the invention is a method of colouring hair which comprises applying to the hair a composition of the invention

[0019] Further provided by the invention in another aspect is the use of a clay to reduce the amount that an agent capable of imparting a colour to hair colours skin relative to the amount that the agent colours hair, wherein the clay has a net charge at its surface and the agent has a net charge which is opposite from that of the clay.

[0020] The invention goes against the conventional teaching, for example as disclosed in US 5,110,318, that anionic and cationic components should not be used together. Indeed, the Laporte Technical Directory for the clay Laponite, "Laponite The Performance Enhancer" states on page 7 that "Laponite products are anionic, and their use in formulations containing cationic compounds is not recommended".

[0021] Surprisingly in the present invention, it is possible to deliver colour to hair whilst reducing skin staining. It is unexpected that skin staining can be reduced whilst still achieving good (and, in some embodiments of the invention, better) delivery of colour to the hair, particularly when the teaching in the art is that clays should not be used with an agent having an opposite charge from that of the clay where delivery of that agent (eg, to hair) is required.

[0022] The invention may have one or more of the further advantages of:

(i) allowing colour to be delivered on a daily basis, for example, from a hair conditioner or shampoo;

(ii) achieving good water-fastness of the colour on the hair ie, good resistance to rinsing with water;

(iii) achieving more effective reversible colouring of the hair compared to the dye used alone (ie, the colour can, if desired, be washed off to some extent with shampoo);

(iv) reducing any toxicity associated with free dye molecules;

(v) imparting good lubrication properties to the hair;

(vi) reducing the need for gloves when the composition is applied; and

(vii) getting reduced rub off of the dye onto fabrics that come into contact with the hair, such as clothes and pillows.

[0023] Compositions of the invention may be intended to be primarily hair colourant products, optionally having secondary benefits such as hair conditioning and/or cleaning properties. Alternatively, the compositions may be intended to be primarily for use in cleaning and/or conditioning hair with colouring representing a secondary benefit. Compositions of the invention may be used to colour all or only part of the hair. For example, the compositions may be used to impart streaks or highlights to hair.

[0024] The clay which is used in the compositions of the invention can be any clay material known in the art. Suitable clays include natural clays, synthetic clays and chemically modified clays. In general, the term clay refers to a compo-

sition comprising fine particles which have a net electrostatic (ie, positive or negative charge) on at least one surface. Preferably, the clay comprises a hydrous silicate of aluminium, magnesium or iron.

[0025] Preferably, the clay has a layered structure. In the compositions of the invention, the clay is advantageously present in the form of a dispersion (for example a sol or gel) or suspension of the clay particles.

[0026] Clays of the invention may be anionic or cationic clays, ie, they may have a net charge on the surface of the clay that is negative or positive, respectively, depending on the nature of the dye which is used. As mentioned above, the term anionic clays and related terms, as used herein, refers to clays which are themselves anionic in nature ie, the clays themselves are negatively charged at their surface and are capable of exchanging cations. Similarly, the term cationic clays and related terms, as used herein, refers to clays which are themselves cationic in nature ie, the clays themselves are positively charged at their surface and are capable of exchanging anions.

[0027] Preferred anionic clays are clays from the smectite class of clays. Typically, clays of this type are crystalline, expandable, three-layer clays.

[0028] Smectite clays are, for example, disclosed in US Patents Nos 3,862,058, 3,948,790, 3,954,632 and 4,062,647 and in EP-A-299,575 and EP-A-313,146, all in the name of Procter & Gamble Company.

[0029] The term smectite clays herein includes both the clays in which aluminium oxide is present in a silicate lattice and the clays in which magnesium oxide is present in a silicate lattice. Typical smectite clay compounds include the compounds having the general formula $Al_2(Si_2O_5)_2(OH)_2 \cdot nH_2O$ and the compounds having the general formula $Mg_3(Si_2O_5)_2(OH)_2 \cdot nH_2O$, and derivatives thereof, for example in which a proportion of the aluminium ions are replaced with magnesium ions or a proportion of the magnesium ions are replaced with lithium ions and/or some of the hydroxyl ions are replaced by fluoride ions; the derivatives may comprise a further metal ion to balance the overall charge. Smectite clays tend to adopt an expandable, three-layer structure.

[0030] Specific examples of suitable smectite clays include those selected from the classes of the montmorillonites, hectorites, volchonskoites, nontronites, saponites, beidelites and sauconites, particularly those having an alkali or alkaline earth metal ion within the crystal lattice structure. Particularly preferred are hectorites, montmorillonites, nontronites, saponites, beidelites, sauconites and mixtures thereof. Most preferred is synthetic hectorite.

[0031] Clays useful in the invention may be three-layer, expandable alumino-silicates which are characterised by a dioctahedral crystal lattice, while the expandable three-layer magnesium silicates have a trioctahedral crystal lattice. Other preferred clays have a mixed tetrahedral/octahedral/tetrahedral co-ordination.

[0032] The anionic clays employed in the compositions of the invention may contain cationic counterions such as protons, sodium ions, potassium ions, calcium ions, magnesium ions, and the like. It is customary to distinguish between clays on the basis of one cation predominantly or exclusively absorbed. For example, a sodium clay is one in which the absorbed cation is predominantly sodium. Such absorbed cations can become involved in exchange reactions with cations present in aqueous solutions. A typical exchange reaction involving a smectite-type clay is expressed by the following equation: $\text{smectite clay}(\text{Na}) + \text{NH}_4\text{OH} \rightarrow \text{smectite clay}(\text{NH}_4) + \text{NaOH}$.

[0033] Since in the foregoing equilibrium reaction, one equivalent weight of ammonium ion replaces an equivalent weight of sodium, it is customary to measure cation exchange capacity (sometimes termed "base exchange capacity") in terms of milliequivalents per 100g of clay (meq/100g). The cation exchange capacity of clays can be measured in several ways, including by electrodialysis, by exchange with ammonium ion followed by titration or by a methylene blue procedure, all as fully set forth in Grimshaw, "The Chemistry and Physics of Clays", pp. 264-265, Interscience (1971). The cation exchange capacity of a clay mineral relates to such factors as the expandable properties of the clay and the charge of the clay, which, in turn, is determined at least in part by the lattice structure, and the like.

[0034] Preferred anionic clays for use in the present invention have an ion exchange capacity of from 0.7 meq/100g to 150 meq/100g. Particularly preferred are clays having an ion exchange capacity of from 30 meq/100g to 100 meq/100g.

[0035] The clays preferably have an average particle size in the range of from 0.0001 μm to 800 μm , more preferably from 0.01 μm to 400 μm such as from 0.02 μm to 220 μm , even more preferably 0.02 μm to 100 μm . Particle sizes can be determined using a Malvern Mastersizer (Malvern Instruments, UK).

[0036] Examples of synthetic hectorites useful in the present invention include those products sold under the trade marks Laponite RD, Laponite RDS, Laponite XLG, Laponite XLS, Laponite D, Laponite DF, Laponite DS, Laponite S and Laponite JS (all from Southern Clay products, Texas, USA, a subsidiary of Rockwood).

[0037] Examples of montmorillonites (also known as bentonites) include: Gelwhite GP, Gelwhite H, Gelwhite L, Mineral Colloid BP, Mineral Colloid MO, Gelwhite MAS 100 (sc), Gelwhite MAS 101, Gelwhite MAS 102, Gelwhite MAS 103, Bentolite WH, Bentolite L10, Bentolite H, Bentolite L, Permونت SX10A, Permонт SC20, and Permонт HN24 (Southern Clay Products, Texas, USA); Bentone EW and Bentone MA (Dow Corning); Bentonite USP BL 670 and Bentolite H4430 (Whitaker, Clarke & Daniels); Clarit 100 G1 and Clarit 1100 G1 (calcium bentonites from Süd Chemie AG); and Volclay 2 (sodium bentonite from Süd Chemie AG).

[0038] Organophilic clays may also be used herein. These are hydrophobically modified clays which have organic ions replacing inorganic metal ions by ion exchange processes known in the art. These kinds of clay are readily miscible

with organic solvents and have the capability to absorb organic solvents at the interlayers. Suitable examples of organophilic clays useful in the invention are Bentone SD-1, SD-2 and SD-3 from Rheox of Highstown, NJ, USA.

[0039] Clays may be used in the present invention either singly or in combination with one or more other clays. If a mixture of clays is used, however, it is preferred that either all of the clays are anionic or all of the clays are cationic. However, mixtures of cationic and anionic clays may be used, provided that the dye remains sufficiently strongly bound to the clay mixture. Clays may be used as obtained from the supplier and may contain conventional additives such as, for example, disintegrating agents (also known as peptisers) and water of hydration.

[0040] Cationic clays suitable for use in the present invention preferably have physical properties (such as structure and particle size) similar to those of the anionic clays mentioned above. The clays are typically layered double hydroxides such as, for example, hydrotalcite. Suitable cationic clays are described in, for example, US 5786381 (Franklin et al), the contents of which are incorporated by reference herein.

[0041] Preferred cationic clays for use in the present invention have an ion exchange capacity of from 0.7meq/100g to 250meq/100g. Particularly preferred are clays having an ion exchange capacity of from 30 meq/100g to 200 meq/100g.

[0042] Examples of cationic clays are the natural or synthetic layered double hydroxide clays. For instance, layered double hydroxides include compounds of formula $[M_{(1-a)}N_a(OH)_2]^{y+} X^{x-}_{y/x} \cdot zH_2O$ where M is selected from divalent metal ions and lithium; N is a trivalent metal ion; X is an anion of charge x^- ; y^+ is the net charge on the mixed metal hydroxide cation; and when M is a divalent metal ion, "a" is a number from 0.17 to 0.5 and $y=a$; and when M is lithium "a" is a number from 0.67 to 0.75 and $y=(2a-1)$; and z is a number from 0 to 10. In these structures, the metal ions occur in layers in which the metal ions are connected together through the OH groups and the anions X, are located in interlayers between layers of metal ions. Furthermore, it is known that X can undergo ion exchange to be replaced by other anions eg organic anions. Various applications for these types of hydroxy materials have been described in the scientific literature, notably including their use as chemical catalysts.

[0043] Examples of cationic clays in the hydrotalcite category include Pural MG30, Pural MG50, Pural MG70 (from Condea Chemie GmbH, Hamburg, Germany). Hydrotalcites commercially available include Sorbacid EXM 911 and Hycite EM 713 (from Süd Chemie AG). Other examples of layered double hydroxides are $Mg_4Al_2(OH)_{12}(SO_4)_{0.8} \cdot xH_2O$ Magaldrate (Guilini) and $Mg_4Al_4(OH)_{12}Cl_2 \cdot xH_2O$ mixed metal hydroxide (Dow Chemicals). Bayerite is also a suitable cationic clay.

[0044] Compositions of the invention contain an agent which is capable of imparting a colour to hair. Such agents have a net positive or negative charge and are typically molecular cations or anions (ie, cations or anions comprising covalent bonds, including for example carbon-carbon bonds), preferably having a molecular weight in the range of from 200 Da to 3000 Da. The agent is normally used in the form of its salt with a charge-balancing counterion. For example, when the agent is positively charged, suitable anions include monovalent anions such as chloride and, when the agent is negatively charged, suitable cations include metal cations such as sodium ions.

[0045] The agent is preferably a cationic or anionic, semi-permanent dye.

[0046] Suitable anionic dyes for use in the present invention, which contain anionic agents, include azo dyes, xanthene dyes and dyes based on carbenium salts. Specific examples of dyes are:

- 6-hydroxy-5-[(4-sulfophenyl)azo]-2-naphthalenesulfonic acid disodium salt (CI 15985; Food Yellow No. 3);
- 2,4-dinitro-1-naphthol-7-sulfonic acid disodium salt (CI 10316; Acid Yellow No. 1; Food Yellow No. 1);
- 2-(2-quinolyl)-1H-indene-1,3(2H)-dione (mixture of mono- and disulfonic acid) (CI 47005; Food Yellow No. 13; Acid Yellow No. 3);
- 4,5-dihydro-5-oxo-1-(4-sulfophenyl)-4-[(4-sulfophenyl)azo]-1H-pyrazole-3-carboxylic acid trisodium salt (CI 19140; Food Yellow No. 4; Acid Yellow No. 23);
- 3',6'-dihydroxyspiro[isobenzofuran-1(3H),9'-(9H)xanthen]-3-one disodium salt (CI 45350; Acid Yellow No. 73; D & C Yellow No. 8);
- 5-[(2,4-dinitrophenyl)amino]-2-phenylaminobenzenesulfonic acid sodium salt (CI 10385; Acid Orange No. 3);
- 4-[(2,4-dihydroxyphenyl)azo]benzenesulfonic acid monosodium salt (CI 14270; Acid Orange No. 6);
- 4-[(2-hydroxy-1-naphthalenyl)azo]benzenesulfonic acid monosodium salt (CI 15510; Acid Orange No. 7);
- 4-[[3-[(2,4-dimethylphenyl)azo]-2,4-dihydroxyphenyl]azo]benzenesulfonic acid monosodium salt (CI 20170; Acid Orange No. 24);
- 4-hydroxy-3-[(4-sulfo-1-naphthalenyl)azo]-1-naphthalenesulfonic acid disodium salt (CI 14720; Acid Red No. 14);
- 7-hydroxy-8-[(4-sulfo-1-naphthalenyl)azo]-1,3-naphthalenedisulfonic acid trisodium salt (CI 16255; Ponceau 4R; Acid Red No. 18);
- 3-hydroxy-4-[(4-sulfo-1-naphthalenyl)azo]-2,7-naphthalenedisulfonic acid trisodium salt (CI 16185; Acid Red No. 27; Food Red 9);
- 5-amino-4-hydroxy-3-(phenylazo)-2,7-naphthalenedisulfonic acid disodium salt (CI 17200; Acid Red No. 33);
- 5-(acetylamino)-4-hydroxy-3-[(2-methylphenyl)azo]-2,7-naphthalenedisulfonic acid disodium salt (CI 18065; Acid

Red No. 35):

3'-6'-dihydroxy-2'-4',5',7'-tetraiodospiro[isobenzofuran-1(3H),9'-[9H]xanthen]-3-one disodium salt (CI 45430; Acid Red No. 51); N-[6-(diethylamino)-9-(2,4-disulfophenyl)-3H-xanthen-3-ylidene]-N-ethylethaneaminium hydroxide internal salt, sodium salt (CI 45100; Acid Red No. 52); 7-hydroxy-8-[[4-(phenylazo)phenyl]azo]-1,3-naphthalenedisulfonic acid disodium salt (CI 27290; Acid Red No. 73);

2'-4',5',7'-tetrabromo-3'-6'-dihydroxyspiro[isobenzofuran-1(3H),9'-[9H]-xanthen]-3-one disodium salt (CI 45380; Acid Red No. 87); 2'-4',5',7'-tetrabromo-4,5,6,7-tetrachloro-3',6'-dihydroxyspiro[isobenzofuran-1(3H),9'-[9H]-xanthen]-3-one disodium salt (CI 45410; Acid Red No. 92);

3'-6'-dihydroxy-4'5'-diiodospiro[isobenzofuran]-1(3H),9'-[9H]-xanthen]-3-one disodium salt (CI 45425; Acid Red No. 95);

Benzenemethanaminium, N-ethyl-N-[4-[[4-ethyl[(3-sulfophenyl)methyl]amino]phenyl](2-sulfophenyl)methylene]-2,5-cyclohexadiene-1-ylidene]-3-sulpho-, hydroxide, inner salt disodium salt, CI 42090; Acid Blue No. 9);

2,2'-(9,10-dihydro-9,10-dioxo-1,4-anthracenediyl)diimino]bis[5-methyl]benzenesulphonic acid disodium salt (CI 61570 Acid Green No. 25);

N-[4-[[4-(diethylamino)phenyl](2-hydroxy-3,6-disulfo-1-naphthalenyl)methylene]-2,5-cyclohexadien-1-ylidene]-N-methylmethanaminium hydroxide internal salt, monosodium salt (CI 44090; Food Green No. 4; Acid Green No. 50);

N-[4-[[4-(diethylamino)phenyl](2,4-disulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene]-N-ethylethanaminium hydroxide internal salt, sodium salt (CI 42045; Food Blue No. 3; Acid Blue No. 1); N-[4-[[4-(diethylamino)phenyl]

(5-hydroxy-2,4-disulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene]-N-ethylethanaminium hydroxide internal salt, calcium salt (2:1) CI 42351; Acid Blue No. 3);

1-amino-4-(cyclohexylamino)-9,10-dihydro-9,10-dioxo-2-anthracenesulfonic acid monosodium salt (CI 62045; Acid Blue No. 62);

2-(1,3-dihydro-3-oxo-5-sulfo-2H-indol-2-ylidene)-2,3-dihydro-3-oxo-1H-indole-5-sulfonic acid disodium salt (CI 73015 Acid Blue No. 74);

9-(2-carboxyphenyl)-3-[(2-methylphenyl)amino]-6-[(2-methyl-4-sulfophenyl)amino]xanthylium hydroxide internal salt, monosodium salt (CI 45190; Acid Violet No. 9);

2-[(9,10-dihydro-4-hydroxy-9,10-dioxo-1-anthracenyl)amino]-5-methylbenzenesulfonic acid monosodium salt (CI 60730 D & C Violet No. 2 Acid Violet No. 43);

bis[3-nitro-4-[(4-phenylamino)-3-sulfophenylamino]phenyl]sulfone (CI 10410; Acid Brown No. 13);

4-amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-naphthalenedisulfonic acid disodium salt (CI 20470; Acid Black No. 1);

3-hydroxy-4-[(2-hydroxynaphth-1-yl)azo]-7-nitro-1-naphthalenesulfonic acid chromium complex (3:2) (CI 15711; Acid Black No. 52);

3-[(2,4-dimethyl-5-sulfophenyl)azo]-4-hydroxy-1-naphthalenesulfonic acid disodium salt (CI 14700; Food Red No. 1; Ponceau SX FD & C Red No. 4);

4-(acetylamino)-5-hydroxy-6-[(7-sulfo-4-[(4-sulfophenyl)azo]-1-naphthalenyl)azo]-1,7-naphthalene disulfonic acid tetrasodium salt (CI 28440, Food Black No. 1); and

3-hydroxy-4-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-ylazo)naphthalene-1-sulfonic acid sodium salt, chromium complex (Acid Red No. 195).

[0047] Agents which are the anionic species in the so-called Acid dyes are particularly preferred.

[0048] Suitable cationic dyes for use in the present invention, which contain cationic agents, include:

3-[(4-amino-6-bromo-5,8-dihydro-1-hydroxy-8-imino-5-oxo-2-naphthyl)amino]-N,N,N-trimethylanilinium chloride (CI 56059; Basic Blue No. 99- Trade name Arianor Steel Blue & Jaracol Steel Blue);

mixture of: 8-[(4-amino-3-nitrophenyl)azo]-7-hydroxy-N,N,N-trimethyl-2-naphthaleneaminium chloride [Major]; 8-[(4-amino-2-nitrophenyl)azo]-7-hydroxy-N,N,N-trimethyl-2-naphthaleneaminium chloride [Minor] (Basic Brown No. 17 - Arianor Sienna Brown & Jaracol Sienna Brown);

8-[(4-aminophenyl)azo]-7-hydroxy-N,N,N-trimethyl-2-naphthaleneaminium chloride (CI 12250; Basic Brown No. 16 - Arianor Mahogany & Jaracol Mahogany); 3-[4,5-dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl]azo]-N,N,N-trimethylanilinium chloride (CI 12719; Basic Yellow No. 57 - Arianor Straw Yellow & Jaracol Straw Yellow); and

7-Hydroxy-8-[(2-methoxyphenyl)azo]-N,N,N-trimethyl-2-naphthaleneaminium chloride (CI 12245; Basic Red No. 76 - Arianor Madder Red & Jaracol Madder Red).

[0049] The dyes mentioned above are available from Warner Jenkinson Europe, Kings Lynn, Norfolk, UK. Jaracol dyes are available from James Robinson Dyes, Huddersfield, UK.

[0050] Other examples of cationic dyes suitable containing cationic agents suitable for use in the invention include:

9-(dimethylamino)benzo[a]phenoxazin-7-ium chloride (CI 51175; Basic Blue No. 6);
 di[4-(diethylamino)phenyl]-[4-(ethylamino)naphthyl]carbenium chloride (CI 42595; Basic Blue No. 7);
 3,7-di-(dimethylaminophenothiazin-5-ium chloride (CI 52015; Basic Blue No. 9);
 di[4-(dimethylamino)phenyl]-[4-(phenylamino)naphthyl]carbenium chloride (CI 44045; Basic Blue No. 26);
 2-[(4-ethyl(2-hydroxyethyl)amino)phenyl]azo]-6-methoxy-3-methylbenzothiazolium methyl sulfate (CI 11154; Basic Blue No. 41);
 bis[4-(dimethylamino)phenyl][4-(methylamino)phenyl]carbenium chloride (CI 42535; Basic Violet No. 1);
 tris-[4-(dimethylamino)phenyl]carbenium chloride (CI 42555; Basic Violet No. 3);
 2-[3,6-(diethylamino)dibenzopyranium-9-yl]benzoic acid chloride (CI 45170; Basic Violet No. 10);
 di(4-aminophenyl)(4-amino-3-methylphenyl)carbenium chloride (CI 42510; Basic Violet No. 14); 1,3-bis[(2,4-diamino-5-methylphenyl)azo]-3-methylbenzene (CI 21010; Basic Brown No. 4); 1-[(4-amino-2-nitrophenyl)azo]-7-(trimethylammonio)-2-naphthol chloride (CI 12251; Basic Brown No. 17); 3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride (CI 50240; Basic Red No. 2);
 1,4-dimethyl-5-[(4-(dimethylamino)phenyl)azo]-1,2,4-triazolium chloride (CI 11055; Basic Red No. 22);
 2-[2-((2,4-dimethoxyphenyl)amino)ethenyl]-1,3,3-trimethyl-3H-indol-1-ium chloride (CI 48055; Basic Yellow No. 11); and
 bis[4-(diethylamino)phenyl]phenylcarbenium hydrogen sulfate (1:1) (CI 42040; Basic Green No. 1).

[0051] Agents which are the cationic species in the so-called Basic dyes are particularly preferred.

[0052] Agents capable of imparting a colour to hair may be used singly or as a mixture of two or more such agents. Preferably, when two or more agents are employed in compositions of the invention, either all of the agents are anionic or all of the agents are cationic.

However, mixtures of anionic and cationic agents and mixtures of anionic and cationic clays may be employed in the invention.

[0053] In the compositions of the invention, the agent and the clay are selected such that they have opposite charges. Thus, cationic agents (for example, cationic dyes) are used together with anionic clays or anionic agents (for example, anionic dyes) are used together with cationic clays. Preferably, the compositions comprise an anionic clay and a cationic dye. Surprisingly, selecting and combining clays in this way provides the advantages of the invention, including low skin staining, whilst giving good delivery of colour to the hair.

[0054] Without wishing to be bound by theory, it is believed that the dye and the clay in the compositions of the invention may form some form of complex in which the dye and the clay are chemically and/or physically bound together, possibly as a result of the opposite charges on the two materials. The dye may be present at the surface of the clay particles and/or within the clay particles, such as by intercalation between layers in the clay particles.

[0055] The amounts of clay and agent are preferably selected such that, in the compositions of the invention, there is sufficient clay at least to balance the charge on the agent. However, this is not essential and a degree of binding of clay to the agent may be effected through polar but uncharged groups at the surface of the clay. Therefore, good results (including reduced skin staining) may be achieved with amounts of clay that are less than the amount that is required to balance the charge on the agent. Similarly, it is possible to use excess clay beyond the amount that balances the charge on the agent. The amount of clay and agent required in a charge-balanced composition can be readily determined: for example, the optimum level of agent and clay can be determined by mixing the agent and the clay (in water), removing the insoluble solids and determining spectrophotometrically the point at which the absorbance of the filtrate or supernatant liquor becomes a minimum with increasing clay content. Formulating the compositions in this way may help to optimise the balance between minimising skin staining and maximising colour delivery to the hair.

[0056] It is particularly preferred that the weight ratio of clay to agent is in the range of from 1:20 to 20:1, preferably 1:10 to 1:0.5. More preferably, the weight ratio of clay to agent is in the range of from 1:5 to 1:0.7, even more preferably from 1:4 to 1:0.9. The ratio of dye to clay used in any given case will depend on factors such as the molecular weight and charge of the dye and the surface area and charge on the clay.

[0057] The amount of clay in compositions of the invention is preferably in the range of from 0.01% to 20% by weight based on total composition, more preferably 0.1% to 10% by weight, most preferably 0.1% to 5% by weight.

[0058] The amount of the agent in compositions of the invention is preferably in the range of from 0.01% to 10% by weight based on total composition, more preferably 0.1% to 5% by weight, most preferably 0.1% to 2% by weight.

[0059] Compositions of the invention may comprise a single combination of a dye and a clay or a mixture of one or more dyes with one or more clays. Mixtures of two or more dye/clay complexes containing different dyes and the same or different clays have been found to be effective in varying the shade of colour imparted to hair.

[0060] Compositions of the invention comprise a perfume and/or a surfactant.

[0061] By the term perfume we mean any component which is added to the composition primarily for the purpose of imparting a fragrance to the composition (although the perfume may also have other functions and/or properties). Perfumes are conventionally added to compositions intended for application to the hair and are well-known to those

skilled in the art. Perfumes may be single compounds or mixtures of two or more different compounds. A perfume will typically be present in the composition of the invention in an amount of from 0.001% to 5% by weight based on total weight of composition, more preferably 0.01% to 2% by weight, even more preferably 0.01% to 1% by weight.

[0062] Surfactants may also be present in compositions of the invention, typically in amounts of from 0.01% to 50% by weight based on total weight of composition, depending on the product form of the composition. Suitable surfactants include anionic, cationic, zwitterionic, amphoteric, non-ionic surfactants and mixtures thereof, and are described in more detail below in connection with specific product forms. The surfactant is selected for compatibility with the clay and agent of the invention and suitable surfactants can be readily identified by those skilled in the art.

[0063] Compositions of the invention are preferably produced by a method which comprises dispersing the clay in an aqueous liquid to form a dispersion and then bringing the agent into contact with the dispersion. The agent may be added to the dispersion of clay or the clay dispersion may be added to the agent. It has been found that such a method provides a composition which has good properties so far as colour delivery to hair and low skin staining are concerned. Preferably, in this method, the agent is in solid form when added to the dispersion eg, in the form of a powdered dye, although solutions of the dye may also be used. The dispersion may be stirred after the agent has been added (eg, for a time of 1 minute to 1 hour at from 10°C to 40°C). Typically, the clay is hydrated in the dispersion before the agent is added; this may require maintaining the clay in the dispersion for a sufficient time and at a sufficient temperature to allow hydration to take place; for example, the clay may be stirred in the aqueous liquid at a temperature of from 10°C to 40°C (preferably 10°C to 30°C) for a time of from 1 minute to 2 hours (preferably 10 minutes to 1 hour). The aqueous liquid may be water or water containing one or more other components (which are preferably water soluble) that are present in the final composition of the invention. Optionally, after the agent has been added to the dispersion, excess aqueous liquid (eg, water) may be removed: for example, by filtration or by centrifuging and withdrawing the supernatant liquor.

[0064] In another aspect, the invention provides a method of colouring hair which comprises applying to the hair a composition of the invention. The method may be primarily or solely intended for colouring the hair, in which case the composition will be a hair colourant composition. Alternatively, the method may achieve one or more other functions besides colouring hair. For example, the composition may be a hair conditioning composition further comprising a hair conditioning agent, in which case the method may also effect conditioning of the hair. Similarly, the composition may be a shampoo composition further comprising a surfactant, in which case the method may also effect cleaning of the hair; shampoo compositions may also condition the hair (eg, if they are so-called 2-in-1 compositions) and, therefore, compositions of the invention may both condition and clean the hair, in addition to colouring the hair.

[0065] When the composition is applied to the hair, the agent and the clay are applied to the hair at the same time ie, simultaneously and in one step. The agent and the clay may be in the form of a preformed complex.

[0066] Compositions of the invention may be used to colour hair in conventional ways eg, by application of the composition to the hair in a specific hair colouring step which may, for example, be employed every two to eight weeks. Preferably, however, the compositions are applied to hair on a regular basis from a rinse-off hair treatment product, for example from twice daily to once every week, as part of a hair cleaning (ie, shampooing) and/or conditioning treatment.

[0067] Compositions of the invention typically contain water, preferably in an amount of from 50% to 99% by weight based on total composition, preferably 50% to 95% by weight, more preferably 75% to 95% by weight. Other solvents, for example alcohols containing from one to four carbon atoms (such as ethanol) may also be present in compositions of the invention.

[0068] The method of the invention may be applied to any type of hair. For example, the method may be applied to pigmented or unpigmented hair eg, white or grey hair. The method may also be used to colour hair which is naturally pigmented or otherwise coloured (eg, by an earlier dyeing step). The method may involve the use of implements such as brushes, applicators, pump action aerosol sprays, combs and the like. It has been found that frictional forces, particularly shear forces, can enhance colour delivery from compositions of the invention, especially from rinse off products.

[0069] Besides the actives, the compositions of the present invention may also contain other ingredients conventionally used in the art such as diluents, sequestrants, thickeners, carriers, surfactants (anionic, cationic, nonionic, amphoteric, zwitterionic and mixtures thereof), antioxidants, proteins, polypeptides, preservatives, moisturising agents, solvents, perfumes, enzymes, polymers and conditioners. Compositions of the invention are rinse off products. Rinse off compositions are compositions that are intended to be rinsed from the hair, typically with water, after use. Most, but not all, of the composition is removed from the hair on rinsing. The compositions are normally rinsed off the hair within 1 hour of application, typically within 30 minutes of application to the hair. Rinse off compositions include shampoos, conditioners and hair colourant compositions.

Shampoo and/or Conditioner Compositions

[0070] Shampoo and/or conditioner compositions are preferred product forms for compositions of the invention, al-

though the compositions may also take other product forms.

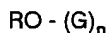
[0071] Shampoo compositions of the invention comprise at least one surfactant which provides a deterging benefit. The deterging surfactant is preferably selected from anionic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

[0072] Suitable anionic surfactants include the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium ammonium and mono-, di- and triethanolamine salts.

[0073] The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

[0074] Nonionic surfactants suitable for use in compositions of the invention may include condensation products of aliphatic (C₈-C₁₈) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups. Other suitable nonionics include mono- or di-alkyl alkanolamides. Example include coco mono- or di- ethanolamide and coco mono-isopropanolamide.

[0075] Further nonionic surfactants which can be included in shampoos for the invention are the alkyl polyglycosides (APGs). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APGs are defined by the following formula:



wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group. Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

[0076] Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

[0077] The surfactants are present in shampoo compositions of the invention in an amount of from 0.1 to 50% by weight of the composition, preferably from 0.5 to 30% by weight.

[0078] Compositions in accordance with the invention may also take the form of hair conditioning compositions, which are rinse off hair conditioning compositions or so-called 2 in 1 compositions containing shampoo and conditioner. The conditioning compositions preferably comprise one or more cationic surfactants. The use of cationic surfactants is especially preferred, because these ingredients are capable of providing conditioning benefits to hair.

[0079] Examples of cationic surfactants include: quaternary ammonium hydroxides, e.g., tetramethylammonium hydroxide, alkyltrimethylammonium hydroxides wherein the alkyl group has from about 8 to 22 carbon atoms, for example octyltrimethylammonium hydroxide, dodecyltrimethylammonium hydroxide, hexadecyltrimethylammonium hydroxide, cetyltrimethylammonium hydroxide, octyldimethylbenzylammonium hydroxide, decyldimethylbenzylammonium hydroxide, stearyldimethylbenzylammonium hydroxide, didodecyldimethylammonium hydroxide, dioctadecyldimethylammonium hydroxide, tallow trimethylammonium hydroxide, cocotrimethylammonium hydroxide, and the corresponding salts thereof, e.g., chlorides, Cetylpyridinium hydroxide or salts thereof, e.g., chloride, Quaternium -5, Quaternium -31, Quaternium -18, and mixtures thereof.

[0080] In hair conditioning compositions according to the invention, the level of cationic surfactant is preferably from 0.01 to 10%, more preferably 0.05 to 5%, most preferably 0.1 to 2% by weight of the composition.

[0081] Hair conditioning compositions of the invention may also contain one or more conditioning agents, preferably selected from silicones, protein hydrolysates and quaternised protein hydrolysates and other materials which are known in the art as having desirable hair conditioning properties.

[0082] Silicones are the most preferred conditioning agents.

[0083] Suitable silicones include volatile and non-volatile silicones, such as for example polyalkylsiloxanes, polyalkylaryl siloxanes, siloxane gums and resins, cyclomethicones, aminofunctional silicones, quaternary silicones and mixtures thereof. Silicone oil is a particularly preferred conditioning agent for hair.

The silicone may be in the form of a low viscosity oil which may contain a high viscosity oil or gum in solution. Alternatively, the high viscosity material may be in the form of an emulsion in water. The emulsion may be of high viscosity oil or of a solution of gum in a lower viscosity oil. The particle size of the oil phase may be anywhere in the range from 30 nanometres to up to 20 microns average size.

[0084] The silicone oil may suitably be a polydimethylsiloxane with an average particle size of less than 20 microns and preferably less than 2 microns. Small particle size enables a more uniform distribution of silicone conditioning agent for the same concentration of silicone in the composition. Advantageously, a silicone with a viscosity in the range 1-20 million cst is used. The silicone can be cross-linked.

[0085] Preferred silicones include polydimethylsiloxanes (of CTFA designation dimethicone) and hydroxylated polydimethylsiloxanes (of CTFA designation dimethiconol). Silicones of the above types are widely available commercially, for example as DC-1784 and DCX2-1391, both ex Dow Corning.

[0086] Suitable protein hydrolysates include lauryl dimonium hydroxy propylamino hydrolysed animal protein, available commercially under the trade name LAMEQUAT L, and hydrolysed keratin containing sulphur-bearing amino acids, available commercially under the trade name CROQUAT WKP.

[0087] In accordance with the invention, the hair shampoo and/or conditioner composition may also comprise a polymeric water-soluble cationic polymer as a conditioning agent.

[0088] The cationic polymer may be present at levels of from 0.01 to 5%, preferably from about 0.05 to 1%, more preferably from about 0.08% to about 0.5% by weight.

[0089] Synthetic or naturally derived polymers having a quaternised nitrogen atom are useful. The molecular weight of the polymer will generally be between 5,000 and 10,000,000 Da, typically at least 10,000 Da and preferably in the range 100,000 to about 2,000,000 Da.

[0090] Representative synthetic quaternised polymers include, for example: cationic copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g., Chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA" as Polyquaternium-16); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11); cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer (referred to in the industry (CTFA) as Polyquaternium 6); mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256; and cationic polyacrylamides as described in WO95/22311.

[0091] Representative naturally-derived quaternised polymers include quaternised cellulosic compounds and cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride. Examples are JAGUAR C-13S, JAGUAR C-15 and JAGUAR-C17, commercially available from Meyhall in their JAGUAR (trademark) series.

[0092] Suitable cationic polyacrylamides are described in WO 95/22311 whose contents are incorporated herein by reference.

[0093] The compositions may further comprise from 0.1 to 5 % by weight of a suspending agent. Examples are polyacrylic acids, cross linked polymers of acrylic acid, copolymers of acrylic acid with a hydrophobic monomer, copolymers of carboxylic acid-containing monomers and acrylic esters, cross-linked copolymers of acrylic acid and acrylate esters, heteropolysaccharide gums and crystalline long chain acyl derivatives. The long chain acyl derivative is desirably selected from ethylene glycol stearates, alkanolamides of fatty acids having from 16 to 22 carbon atoms and mixtures thereof. Polyacrylic acid is available commercially as Carbopol 420, Carbopol 488 or Carbopol 493. Polymers of acrylic acid cross-linked with a polyfunctional agent may also be used, they are available commercially as Carbopol 910, Carbopol 934, Carbopol 940, Carbopol 941 and Carbopol 980. An example of a suitable copolymer of a carboxylic acid containing a monomer and acrylic acid esters is Carbopol 1342. All Carbopol materials are available from Goodrich and Carbopol is a trade mark. A further suitable suspending agent is dihydrogenated tallow phthalic acid amide (available from Stepan under the trademark Stepan TAB-2).

[0094] Suitable cross linked polymers of acrylic acid and acrylate esters are Pemulen TR1 or Pemulen TR2. A suitable heteropolysaccharide gum is xanthan gum, for example that available as Kelzan mu.

[0095] Another ingredient that may advantageously be incorporated into shampoo and/or conditioning compositions of the invention is a fatty alcohol material. The use of these materials is especially preferred in conditioning compositions of the invention, in particular conditioning compositions which comprise one or more cationic surfactant materials. The combined use of fatty alcohol materials and cationic surfactants in conditioning compositions is believed to be especially advantageous, because this leads to the formation of a lamellar phase, wherein the cationic surfactant is dispersed.

[0096] Preferred fatty alcohols comprise from 8 to 22 carbon atoms, more preferably 16 to 20. Examples of preferred fatty alcohols are cetyl alcohol and stearyl alcohol. The use of these materials is also advantageous in that they contribute to the overall conditioning properties of compositions of the invention.

[0097] The level of fatty alcohol materials is conveniently from 0.01 to 10%, preferably from 0.1 to 5% by weight of the composition. The weight ratio of cationic surfactant to fatty alcohol is preferably from 10:1 to 1:10, more preferably from 4:1 to 1:8, most preferably from 1:1 to 1:6.

[0098] A further ingredient that may be desirably included in the shampoo and/or conditioning compositions is a pearlescent material. Suitable pearlescent materials include ethylene glycol distearate, ethylene glycol monostearate, guanine and titanium dioxide coated micas, bismuth oxychloride, and stearic monoethanol amide. The level of pearlescent material present in the composition is generally 0.1% to 5%, preferably from 0.3% to 3% by weight of the

composition.

[0099] The shampoo and/or conditioner compositions of the invention are preferably aqueous based. The compositions suitably comprise water in amount of from about 20 to about 99% by weight of the total composition.

[0100] The invention will now be described, by way of nonlimiting example only, with reference to the following examples. In the examples and throughout this specification, all references to percentages are to percentages by weight unless indicated otherwise.

EXAMPLES

Examples 1 to 9

[0101] Laponite XLS (3% w/w) was added to water (96%) and stirred with an impeller at 300 rpm for 30 minutes until the solution became clear. 1% w/w Arianor Mahogany dye powder (Warner Jenkinson, Norfolk, UK) was added and stirred for a further 30 minutes. The resulting dye/clay complex was concentrated by removing excess water by filtration under vacuum or by centrifuging and withdrawing the supernatant liquor.

[0102] The following are examples of hair conditioner compositions containing the dye/clay complex thus prepared.

Example				1	2	3
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100
Dye/clay complex			Colourant	4	4	4
Behenyl trimethyl ammonium chloride	Genamin KDM-P	Clairant	cationic surfactant	1	-	-
Ditallow dimethyl ammonium chloride and propylene glycol	Arquad 2HT75	Akzo	cationic surfactant	-	1	0.3
Cetrimonium chloride	Genamine CTAC	Hoescht	cationic surfactant		-	0.7
Behenyl alcohol			fatty alcohol	5	-	-
Stearyl alcohol	Conol 30s	New Japan Chem .	fatty alcohol	-	-	-
Cetostearyl alcohol	Nacol 16-18	Condea	fatty alcohol	-	3	3
Silicone emulsion	DC2-1784	Dow Corning	conditioning ingredient	2	-	-
Silicone emulsion	DC 1786	Dow Corning	conditioning ingredient	-	2	-
Disodium EDTA			sequesterant	0.1	0.1	0.1
Methyl paraben	Nipagin	Nipa Lab	preservative	0.2	0.2	0.2
Perfume			fragrance	0.5	0.5	0.5

Example				4	5	6
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100
Dye/clay complex			Colourant	4	4	4
Behenyl trimethyl ammonium chloride	Genamin KDM-P	Clairant	cationic surfactant	1	-	-
Ditallow dimethyl ammonium chloride and propylene glycol	Arquad 2HT75	Akzo	cationic surfactant	-	-	5
Cetrimonium chloride	Genamine CTAC	Hoescht	cationic surfactant	-	1	
Behenyl alcohol			fatty alcohol	3	-	
Stearyl alcohol	Conol 30s	New Japan Chem .	fatty alcohol	-	2.5	
Cetostearyl alcohol	Nacol 16-18	Condea	fatty alcohol	-	1.5	
Silicone emulsion	DC2-1784	Dow Corning	conditioning ingredient	-	-	1.5
Silicone emulsion	DC 1786	Dow Corning	conditioning ingredient	2	-	
Disodium EDTA			sequesterant	0.1	0.1	0.1
Methyl paraben	Nipagin	Nipa Lab	preservative	0.2	0.2	0.2
Perfume			fragrance	0.5	0.5	0.5

Example				7	8	9
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100
Dye/clay complex	Lexamine S-13	Inolex	Colourant	3	3	3
PEG-2 Oleammonium Chloride and propylene glycol	Ethoquad 0/12 PG	Akzo	cationic surfactant	-	2	1
Ditallow dimethyl ammonium chloride and propylene glycol	Arquad 2HT75	Akzo	cationic surfactant	0.24	-	-
Cetrimonium chloride	Genamine CTAC	Hoescht	cationic surfactant	0.56	-	-
Stearamidopropyl Dimethylamine			conditioner		0.75	0.75
Behenyl trimethyl ammonium methosulphate and cetearyl alcohol	Incroquat Behenyl TMS	Croda	conditioner	-	1	1
Stearyl alcohol	Conol 30s	New Japan Chem .	fatty alcohol	-	2	2
Cetostearyl alcohol	Nacol 16-18	Condea	fatty alcohol	3	3	2
Cyclopentasiloxane	DC 245	Dow corning	conditioner	-	2	2.5
Silicone emulsion	DC 1786	Dow Corning	Conditioning ingredient	1.5	2.0	1.5
Citric acid	citric acid		pH adjuster	-	0.245	0.245
Disodium EDTA			Sequestrant	0.1	0.1	0.1
Methyl paraben	Nipagin	Nipa Lab	Preservative	0.2	0.2	0.2
Perfume			fragrance	0.5	0.5	0.5

[0103] The compositions of Examples 1 to 9 can be produced as follows:

[0104] The cationic surfactant is dissolved in water at 90°C. The fatty alcohols are pre-melted at about 60°C. The molten fatty alcohols are added to the cationic surfactant solution at 70°C and a shear force is applied (Silverson L4R) for 30 minutes. The mixture is cooled slowly and the dye/clay complex, the silicone emulsion, perfume and ancilliary ingredients are added at a temperature below 45°C.

Example 10

[0105] Mixtures of Mahogany dye, Laponite XLS and water were prepared according to the method described above. Thus, Laponite XLS was added to water and stirred with an impeller at 300 rpm for 30 minutes until the solution became clear and the Mahogany dye powder was added and stirred for a further 30 minutes. Compositions containing 1% by

weight dye, various amounts of Laponite XLS and balance water were prepared.

[0106] The compositions were assessed for their colour delivery by application of 0.15g of composition for 60 seconds to switches (also known as tresses or swatches) of yak hair (International Hair Importers and Products, Inc, NY, USA), followed by rinsing with water for 60 s and analysis of the treated hair by reflectometer (ColorQuest, HunterLab, VA, USA) and the following results were obtained:

% w/w Laponite XLS	Change in colour (ΔE)
0	25
0.5	27
1.0	32
2.5	39
3.0	41
5.0	38
10	18
12.5	23
15	20

[0107] Thus, good colour delivery to the hair is seen throughout the compositions tested, with surprisingly good delivery at lower levels of Laponite XLS beyond the levels achieved by the use of the dye alone.

[0108] The same compositions were assessed for their skin staining properties in vitro by application of 0.25 g of composition for 60 s, rubbed in for 30 s and left to stand for 30 s, followed by rinsing in 1 litre of water for 60 s, to samples of skin obtained from IMS Inc, Milford CT, USA. The change in colour was again determined using a reflectometer.

% w/w Laponite XLS	Change in colour (ΔE)
0.5	64
1.0	61
2.5	11
3.0	12
5.0	8
10	2
12.5	2
15	2

[0109] Thus, skin staining was greatly reduced for compositions containing the clay in an amount of 2.5% by weight and above, whilst, as shown above, the levels of hair colouration were maintained.

Example 11

[0110] A dye/clay complex containing Mahogany dye and Laponite XLS clay at a weight ratio of 1 dye: 2.5 clay was prepared according to the procedure described above.

[0111] The dye/clay complex was formulated as a 0.2% by weight dye/ 0.5% by weight clay hair conditioning composition in water also comprising 1% by weight behenyl trimethylammonium chloride (BTAC) and 6% by weight behenyl alcohol or 1% by weight ditallow dimethyl ammonium chloride (Diquat) and 3% by weight cetostearyl alcohol according to the procedure described above. The compositions were applied to switches of yak hair and the change in colour was determined using a reflectometer. The change in colour was compared to compositions containing the same level of dye and dye/clay complex alone (in water) after rinsing the product from the hair. The results are as follows:

Treatment	Change in colour (ΔE)
0.2% Mahogany dye solution	19.8
0.2% Dye/0.5% clay complex alone	24.6
Dye/clay complex with 1% BTAC /6% behenyl alcohol	15.9
Dye/clay complex with 1% Diquat /3% cetostearyl alcohol	15.9

[0112] Thus the dye/clay complex can be effectively delivered to the hair from a rinse-off daily hair treatment product.

[0113] The same complexes and compositions of the invention showed a reduction in skin staining as shown below.

Treatment	Skin Staining (ΔE)
0.2% Mahogany dye solution	58.1
0.2% Dye/0.5% clay complex alone	10.1
Dye/clay complex with 1% BTAC /6% behenyl alcohol	8.4
Dye/clay complex with 1% Diquat /3% cetostearyl alcohol	9.1

Example 12

[0114] Example 3 was repeated using Mahogany dye complexed with bentonite at a weight ratio of dye to clay of 1:3. The results of colour delivery on hair and skin staining were as follows.

Treatment	Change in colour (ΔE)
1% wt Mahogany dye	20.8
1% dye/ 3% clay complex alone	16.1
Dye/clay complex in Example 3	10.3

[0115] The same complexes and compositions of the invention showed a reduction in skin staining as shown below.

Treatment	Skin Staining(ΔE)
1% wt Mahogany dye	65.4
1% dye/ 3% clay complex alone	21.5
Dye/clay complex in Example 3	8.3

Example 13

[0116] Example 12 was repeated using Bentone EW, an organically modified clay, in place of bentonite. Compositions were formulated as 2:1 and 1:1 by weight clay to dye dispersions in water at 3% complex by weight and 2% complex by weight, respectively. The 1:1 composition was as good as the corresponding composition containing Laponite XLS in place of Bentone EW at delivering colour to the hair.

Examples 14 to 23

[0117] Anionic dye/cationic clay complexes were prepared according to Examples 26-29. Anionic clay/cationic dye complexes were prepared according to Examples 11 and 12. The following are examples of shampoo compositions incorporating the previously mentioned dye clay complexes according to the invention:

Example				14	15	16
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100
Dye clay complex				1 ¹⁾	0.7 ²⁾	0.7 ²⁾
Sodium Lauryl Ether Sulphate	Empicol ESB70	Albright & Wilson	surfactant	14		
Decyl polyglucose	Plantaren 2000 UP	Henkel	surfactant		6	6
Sodium Lauroyl-2-lactylate	Pationic 138C	RITA	surfactant			6
Cocamidopropyl-N-2-hydroxyethyl carbomoyl methyl dimethyl ammonium chloride	Montaline C40	Seppic	surfactant			
Sodium lauramphoacetate	Mackam 1L-30	McIntyre	surfactant			
Cetrimonium chloride	Arquad 16-50	Akzo	surfactant			
Behenyl alcohol	Nacol 22-97	Condea	conditioner			
Polydimethyl siloxane emulsion	DC2-1310	Dow Corning	conditioner			
POE Alkylamide sulphate	Sunamide C-3	NOF	surfactant			
C9-11 alcohol (8EO) ethoxylate	Neodol 91-8E	Shell	surfactant			
Cocamidopropyl betaine	Tegobetaine CK	Goldschmidt	surfactant	2		
Sodium Chloride	Sodium chloride		viscosity modifier	1		
Methyl paraben	Nipagin	Nipa Lab	preservative	0.2	0.2	0.2
Perfume			fragrance	0.5	0.5	0.5

1) Brilliant Black BN: Dow Mixed Metal Hydroxide 1:4 ratio

2) Mahogany : Laponite XLS 1:2.5 ratio

3) Mahogany : Bentonite 1: 3 ratio

4) Brilliant Black BN: Pural MG30 1:5 ratio

5) External D&C Violet No 2: Dow mixed metal hydroxide 1:3 ratio

Example				17	18	19
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100
Dye clay complex				0.7 ²⁾	0.7 ²⁾	0.7 ²⁾
Sodium Lauryl Ether Sulphate	Empicol ESB70	Albright & Wilson	surfactant			
Decyl polyglucose	Plantaren 2000 UP	Henkel	surfactant			
Sodium Lauroyl-2-lactylate	Pationic 138C	RITA	surfactant			
Cocamidopropyl-N-2-hydroxyethyl carbomoyl methyl dimethyl amonium chloride	Montaline C40	Seppic	surfactant	4	4	
Sodium lauramphoacetate	Mackam 1L-30	McIntyre	surfactant	0.56	0.56	
Cetrimonium chloride	Arquad 16-50	Akzo	surfactant		1	
Behenyl alcohol	Nacol 22-97	Condea	conditioner		9.8	
Polydimethyl siloxane emulsion	DC2-1310	Dow Corning	conditioner		0.3	
POE Alkylamide sulphate	Sunamide C-3	NOF	surfactant			8
C9-11 alcohol (8EO) ethoxylate	Neodol 91-8E	Shell	surfactant			4
Cocamidopropyl betaine	Tegobetaine CK	Goldschmidt	surfactant			4
Sodium Chloride	Sodium chloride		viscosity modifier			
Methyl paraben	Nipagin	Nipa Lab	preservative	0.2		0.2
Perfume			fragrance	0.5		0.5

Example				20	21	22	23
Ingredient	Trade name	Supplier	Function	%w/w	%w/w	%w/w	%w/w
Deionised water			solvent	q.s. to 100	q.s. to 100	q.s. to 100	q.s. to 100
Dye clay complex				1 ¹⁾	1.2 ³⁾	0.6 ⁴⁾	0.4 ⁵⁾
Sodium Lauryl Ether Sulphate	Empicol ESB70	Albright & Wilson	surfactant				
Decyl polyglucose	Plantaren 2000 UP	Henkel	surfactant				
Sodium Lauroyl-2-lactylate	Pationic 138C	RITA	surfactant				
Cocamidopropyl-N-2-hydroxyethyl carbamoyl methyl dimethyl ammonium chloride	Montaline C40	Seppic	surfactant				
Sodium laurylamphoacetate	Mackam 1L-30	McIntyre	surfactant				
Cetrimonium chloride	Arquad 16-50	Akzo	surfactant				
Behenyl alcohol	Nacol 22-97	Condea	conditioner				
Polydimethyl siloxane emulsion	DC2-1310	Dow Corning	conditioner				
POE Alkylamide sulphate	Sunamide C-3	NOF	surfactant	8	8	8	8
C9-11 alcohol (8EO) ethoxylate	Neodol 91-8E	Shell	surfactant	4	4	4	4
Cocamidopropyl betaine	Tegobetaine CK	Goldschmidt	surfactant	4	4	4	4
Sodium Chloride	Sodium chloride		viscosity modifier				
Methyl paraben	Nipagin	Nipa Lab	preservative	0.2	0.2	0.2	0.2
Perfume			fragrance	0.5	0.5	0.5	0.5

[0118] The shampoo formulations were tested for colour delivery by treating human natural white with 0.15 g of composition rubbed through a hair switch for 60 s, followed by rinsing with water for 60 s. The compositions showed colour delivery onto hair as follows:

Treatment	Change in colour(ΔE)
Example 14	2.8
Example 15	9.0

(continued)

Treatment	Change in colour(ΔE)
Example 16	5.9
Example 17	11.9
Example 18	15.2
Example 19	2.1
Example 20	6.8
Example 21	3.7
Example 22	5.1
Example 23	4.0

[0119] The same complexes and compositions of the invention showed a reduction in skin staining compared to the same composition with an equal amount of free dye.

[0120] Furthermore, Example 17 showed a build up of colour over several wash cycles as shown below:

Treatment	Change in colour(ΔE)
1 Wash cycle with Example 17	11.9
2 Wash cycles with Example 17	16.4
3 Wash cycles with Example 17	19.0
4 Wash cycles with Example 17	21.9

Example 24

[0121] Example 3 was repeated using human natural white hair and a dye/clay complex was prepared using 1g Madder Red dye for every 2g Laponite XLS. Colour delivery from the hair conditioning composition onto hair was of the same order as delivery from an equal concentration of the dye in the hair conditioning composition. Reduced skin staining was observed when the dye/clay complex was incorporated in a hair conditioning composition compared to the same amount of free dye in the hair conditioning composition as shown below:

Treatment	ΔE) Change in colour	(ΔE)Skin Staining
0.8% Madder Red	24.2	26.3
0.8% Madder Red/clay complex	21.5	10.7

[0122] Madder Red dye is a dye of limited solubility. Using the dye in the form of a dye/clay complex according to the invention allowed a greater amount of dye to be used in the compositions ie, the amount of dye that could be used was no longer limited by the solubility of the dye in water.

Treatment	Change in colour (ΔE)
0.8% Madder Red in water	23.7
0.8% Madder Red/clay complex	40.8

Example 25

[0123] Example 24 was repeated using anionic hectorite clay containing fluoride ions (Laponite JS) and Steel Blue dye at a dye to clay weight ratio of 1:2. The complex showed delivery of colour to the hair from a conditioner composition, with reduced skin staining compared to the uncomplexed dye in an otherwise identical hair conditioning composition as shown below.

Treatment	Change in colour (ΔE)
0.2% w/w Steel Blue in Example 8	11.5
0.2% w/w Steel Blue/clay complex in Example 8	11.1
1% w/w Steel Blue Solution	25.0

(continued)

Treatment	Change in colour (ΔE)
1% w/w Steel Blue/clay complex	26.3

Treatment	(ΔE)Skin Staining
1% w/w Steel Blue in Example 8	34.4
1% w/w Steel Blue/clay complex in Example 8	12.0

Example 26

[0124] Complexes containing cationic clays were prepared as follows.

[0125] 2.79g of Pural MG30 was added to 46.71g of water in a 100 ml beaker. 0.5g of dye (either Brilliant Black BN or Ext D&C Violet No. 5) was then added and the mixture was homogenised for 30 mins at 24,000 rpm using an UltraTurax mixer (IKA) fitted with a T25 dispersing tool. The resulting 1:5.5 weight ratio dye:clay mixture was then added to the hair conditioning composition base in the manner previously described.

[0126] The complexes were applied to hair from a hair conditioning composition containing a cationic hair conditioning agent. Colour delivery to human natural white hair is shown below:

Treatment (% by wt)	(ΔE) Change in colour	(ΔE)Skin Staining
0.1% Ext D&C Violet No. 2 in Example 2	8.6	-
0.1% Ext D&C Violet No. 2/ clay complex in Example 2	18.0	-
0.1% Brilliant Black BN in Example 2	25.1	64.4
0.1% Brilliant Black BN/ clay complex in Example 2	21.4	4.8

[0127] Thus the hair conditioner composition containing the clay complex with Ext D&C Violet No. 2 showed better colour delivery than the corresponding conditioner with free dye. The colour delivery for the conditioner containing Brilliant Black BN was slightly higher than that shown by the Brilliant Black BN complex. However, the conditioner composition containing Brilliant Black BN dye showed reduced stability in terms of its structure and produced much higher skin staining.

Example 27

[0128] 2.0g of Layered double hydroxide (Dow Mixed metal hydroxide) was added to 47.5g of water in a 100 ml beaker. 0.5g of Brilliant Black BN was then added and the mixture was homogenised for 5 mins at 11,000 rpm using an UltraTurax mixer (IKA) fitted with a T25 dispersing tool. The resulting 1:4 weight ratio dye:clay mixture was then added to the conditioner base in the manner previously described.

[0129] The dye/clay complex alone or once incorporated into Example 3 showed good colour delivery to human natural white hair as illustrated below:

Treatment (% by wt)	Change in colour (ΔE)
0.2% Brilliant Black BN in water	3.3
0.2% Brilliant Black BN/clay complex only	28.6
0.2% Brilliant Black BN/clay complex in Example 3	10.8 (2.4 skin staining)

Example 28

[0130] Example 27 was repeated using Magaldrate (Giulini, Corp NJ, USA) as the clay.

Example 29

[0131] 1.5g of Layered double hydroxide was added to 48g of water in a 100 ml beaker. 0.5g of Ext D&C Violet No 2 was then added and the mixture was homogenised for 5 mins at 11,000 rpm using an UltraTurax mixer (IKA) fitted with a T25 dispersing tool. The resulting 1:3 weight ratio dye:clay mixture was then added to the conditioner base in the manner previously described.

[0132] The dye/clay complex alone or once incorporated into a formulation according to Example 3 (but with the different dye/clay complex) showed good colour delivery to human natural white hair as illustrated below:

Treatment (% by weight)	Change in colour (ΔE)
0.2% Ext D&C Violet No 2 in water 0.2% Ext D&C Violet No 2/clay complex only 0.2% Ext D&C Violet No 2/clay complex in Example 3	4.3 22.4 8.4

Claims

1. Rinse off hair colouring composition comprising:

(i) a clay having a net positive or negative charge at its surface;

(ii) an agent capable of imparting a colour to hair; and

(iii) a perfume and/or a surfactant,

wherein the agent has a net charge which is opposite from the charge on the surface of the clay.

2. Composition as claimed in Claim 1, wherein the clay has a layered structure.

3. Composition as claimed in Claim 1 or Claim 2 wherein the clay is present in the form of a dispersion or suspension of clay particles.

4. Composition as claimed in any one of the preceding claims, which contains at least sufficient clay to balance the charge on the agent.

5. Composition as claimed in any one of the preceding claims, wherein the weight ratio of clay to agent is in the range of from 1:10 to 1:0.5.

6. Composition as claimed in Claim 5; wherein the weight ratio of clay to agent is in the range of from 1:5 to 1:0.7.

7. Composition as claimed in any one of the preceding claims, wherein the agent is a molecular cation or a molecular anion.

8. Composition as claimed in any one of the preceding claims, wherein the clay is an anionic clay and the agent is a cationic dye.

9. Composition as claimed in Claim 8, wherein the clay is from the smectite class of clays.

10. Composition as claimed in Claim 9, wherein the clay is a natural, synthetic or chemically modified clay of the type selected from the group consisting of hectorite, montmorillonite, nontronite, saponite, beidelite, sauconite and mixtures thereof.

11. Composition as claimed in Claim 10, wherein the clay is synthetic hectorite.

12. Composition as claimed in any one of Claims 8 to 11, wherein the agent is the cation of a Basic dye.

13. Composition as claimed in any one of Claims 1 to 7, wherein the clay is a cationic clay and the agent is an anionic dye.
14. Composition as claimed in Claim 13, wherein the clay is a natural or synthetic layered double hydroxide clay.
15. Composition as claimed in Claim 13 or Claim 14, wherein the agent is the anion of an Acid dye.
16. Composition as claimed in any one of the preceding claims which is a hair colourant composition.
17. Composition as claimed in any one of the preceding claims which is a hair conditioning composition comprising a hair conditioning agent.
18. Composition as claimed in any one of Claims 1 to 17 which is a shampoo composition further comprising a surfactant.
19. Method of producing a composition of any one of Claims 1 to 18 which comprises dispersing the clay in an aqueous liquid to form a dispersion and then bringing the agent into contact with the dispersion.
20. Method as claimed in Claim 19 wherein the clay is hydrated before the agent is added.
21. Method of colouring hair which comprises applying to the hair a composition as claimed in any one of Claims 1 to 18.
22. Use of a clay to reduce the amount that an agent capable of imparting a colour to hair colours skin relative to the amount that the agent colours hair, wherein the clay has a net charge at its surface and the agent has a net charge which is opposite from that of the clay.
23. Use as claimed in Claim 22, wherein the clay is an anionic clay and the agent is a cationic dye molecule.
24. Use as claimed in Claim 22, wherein the clay is a cationic clay and the agent is an anionic dye molecule.



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EUROPEAN SEARCH REPORT

Application Number
EP 02 25 7733

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,D Y	DE 40 20 272 A (HENKEL KGAA) 2 January 1992 (1992-01-02) * page 2, line 41 - line 55 * * page 3, line 22 - line 29 * * page 4, line 34 - line 35; claims 1,7,13; examples *	1,2,4-6, 13-15 16-21	A61K7/13 A61K7/06
X,D Y	US 4 402 698 A (KALOPISSIS GREGOIRE ET AL) 6 September 1983 (1983-09-06) * column 2, line 8 - line 43; claims 1,8,10,19,21,23 * * column 3, line 64 - column 4, line 20 * * column 5, line 9 - line 29 * * column 7, line 60 - column 8, line 18; example 6 *	22-24 16-21	
X	DATABASE WPI Section Ch, Week 197621 Derwent Publications Ltd., London, GB; Class A97, AN 1976-38920X XP002197917 & JP 51 041443 A (KOBAYASHI KOSE KK), 7 April 1976 (1976-04-07) * abstract *	1-4,7-11	TECHNICAL FIELDS SEARCHED (Int.Cl.7) A61K
X,D	PATENT ABSTRACTS OF JAPAN vol. 003, no. 087 (C-053), 25 July 1979 (1979-07-25) & JP 54 064644 A (SHISEIDO CO LTD), 24 May 1979 (1979-05-24) * abstract *	1-4, 7-11,16, 22,23	
-/--			
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 10 March 2003	Examiner Pregetter, M
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	



European Patent
Office

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Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (INCL.7)
X	DATABASE WPI Section Ch, Week 197926 Derwent Publications Ltd., London, GB; Class D21, AN 1979-48186B XP002197918 & JP 54 063132 A (SHISEIDO CO LTD), 21 May 1979 (1979-05-21) * abstract *	1-4, 7-10,16, 22,23	
A	FR 2 549 721 A (SECTA LABO COSMETOLOGIE Y ROCH) 1 February 1985 (1985-02-01) * page 4, line 1 - line 22; claims 1,8,10 * * page 9, line 31 - page 13, line 25; examples 6,10,15 *	1-24	
A	EP 0 823 250 A (SHISEIDO COMPANY LIMITED) 11 February 1998 (1998-02-11) * page 4, line 16 - line 26 * examples 1-8 and 1-9 * page 3, line 36 - line 43; claims 1,2 *	1-21	
A	US 5 902 591 A (HERSTEIN MORRIS) 11 May 1999 (1999-05-11) * column 3, line 24 - column 4, line 30; claims 6,9,10; example 2 *	1-21	
<div style="text-align: center;">TECHNICAL FIELDS SEARCHED (Int.Cl.7)</div>			
<div style="text-align: center;">The present search report has been drawn up for all claims</div>			
Place of search MUNICH		Date of completion of the search 10 March 2003	Examiner Pregetter, M
<div style="display: flex; justify-content: space-between;"> <div> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> </div> <div> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p> </div> </div>			

EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 7733

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10-03-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 4020272	A	02-01-1992	DE 4020272 A1	02-01-1992
			WO 9200355 A1	09-01-1992

US 4402698	A	06-09-1983	LU 81994 A1	23-07-1981
			LU 82581 A1	17-02-1982
			AR 227771 A1	15-12-1982
			AT 381021 B	11-08-1986
			AT 607480 A	15-01-1986
			BE 886624 A1	12-06-1981
			CA 1168584 A1	05-06-1984
			CH 646050 A5	15-11-1984
			DE 3046964 A1	03-09-1981
			FR 2471779 A1	26-06-1981
			GB 2065177 A ,B	24-06-1981
			GR 72510 A1	16-11-1983
			IT 1193719 B	24-08-1988
			JP 56092815 A	27-07-1981
			MX 153825 A	19-01-1987
			NL 8006753 A	16-07-1981
			US 4545978 A	08-10-1985

JP 51041443	A	07-04-1976	JP 932896 C	14-11-1978
			JP 52007065 B	26-02-1977

JP 54064644	A	24-05-1979	JP 1064138 C	22-09-1981
			JP 55050005 B	16-12-1980

JP 54063132	A	21-05-1979	JP 1390642 C	23-07-1987
			JP 61049349 B	29-10-1986

FR 2549721	A	01-02-1985	FR 2549721 A1	01-02-1985
			AT 37786 T	15-10-1988
			AU 570706 B2	24-03-1988
			AU 3119884 A	31-01-1985
			BE 900219 A1	25-01-1985
			DE 3474509 D1	17-11-1988
			DE 133129 T1	14-08-1985
			DK 364184 A	29-01-1985
			EP 0133129 A2	13-02-1985
			ES 8503942 A1	01-07-1985
			FI 842959 A	29-01-1985
			IT 1209571 B	30-08-1989
			JP 60084212 A	13-05-1985
			NO 843031 A	29-01-1985

EP 0823250	A	11-02-1998	JP 10067624 A	10-03-1998

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 02 25 7733

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-03-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0823250 A		EP 0823250 A2	11-02-1998
		JP 10101537 A	21-04-1998
		TW 434026 B	16-05-2001
		US 5817155 A	06-10-1998
US 5902591 A	11-05-1999	EP 1037585 A1	27-09-2000
		JP 2002512604 T	23-04-2002
		WO 9843598 A2	08-10-1998